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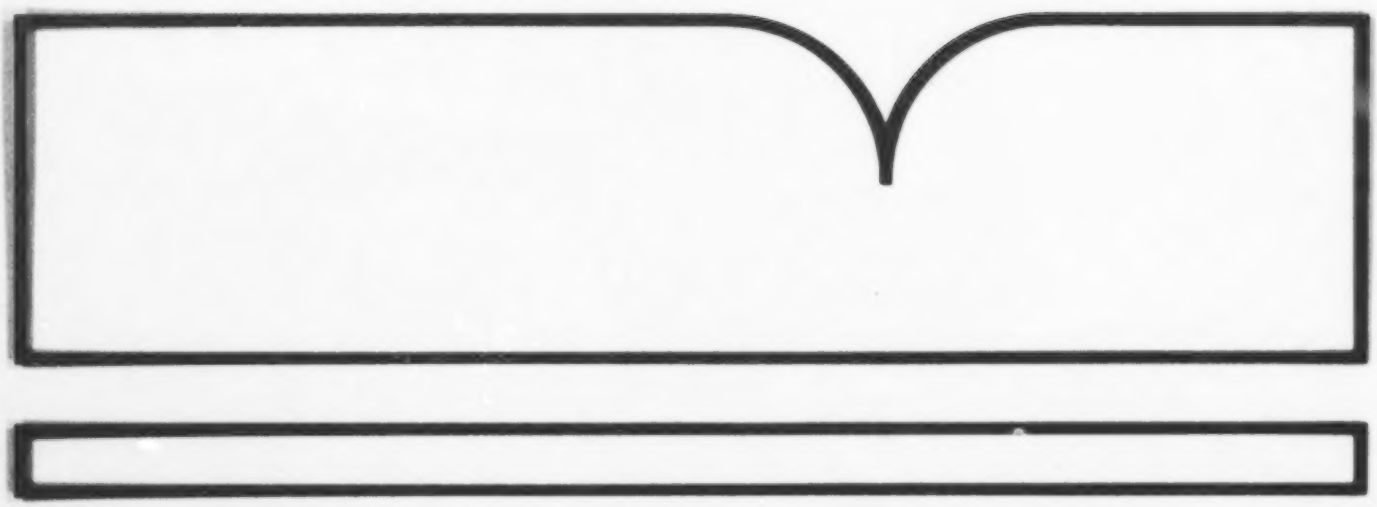

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CALCIUM-BASED SORBENTS IN THE LIMB PROCESS

by

David A. Kirchgessner, Robert V. Hendriks,
and Norman Kaplan
U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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ABSTRACT

EPA research on dry sorbent injection, which began in the late 1960's and early 1970's, will be demonstrated as the limestone injection multi-stage burner (LIMB) process at Ohio Edison's Edgewater plant in 1987. The effect and interrelationship of fundamental sorbent properties are now fairly well understood. These considerations, along with pilot-scale furnace testing, suggest that commercial calcium hydroxide will be the sorbent of choice for the demonstration. Ongoing research at EPA is focused on the modification of commercial sorbents to make them more reactive with SO_2. Changes in calcination and hydration conditions, and the addition of dispersants to the water of hydration, have shown promise.

The boiler conditions necessary for effective SO_2 capture have been defined, and the Edgewater boiler has been well characterized with respect to sulfation temperature window, quench rate, flow pattern, and injection location. The effects of sorbent injection on boiler efficiency, particulate collection, and solid waste handling and disposal have been studied, and negative effects can apparently be remedied by available techniques.

INTRODUCTION

During the late 1960's and early 1970's, the Environmental Protection Agency (EPA) and its predecessor organizations studied air pollution systems for coal-fired utility boilers. This early work produced developments such as flue gas desulfurization (FGD) and low nitrogen oxide (NO_x) combustion technology, including the multistage burner which will be used in the limestone injection multistage burner (LIMB) process.[1, 2]

The forerunner of FGD was dry limestone ($CaCO_3$) injection into the boiler firebox, either above the flame zone or through the burner with the coal. The research associated with this process culminated in a demonstration at TVA's Shawnee plant in 1970. The best sulfur capture obtained with limestone was 36 percent with the boiler running at only half load. Sulfur capture at higher loads, using limestone as the sorbent, dropped to the range of 17 to 20 percent.[3] This relatively poor performance was attributed to one of several factors: 1) overburning of the sorbent at high temperatures; 2) poor mixing of the sorbent with the combustion gases; 3) chemical deactivation of the sorbent by mineral matter in the coal; and 4) unfavorable time/temperature environments for the sorbent and for reaction kinetics.

It was not until the late 1970's that research developments renewed interest in dry sorbent injection. Energy and Environmental Research

Corporation (EERC) conducted a short series of experiments using limestone sorbents in conjunction with a distributed mixing burner, one type of multistage burner.[4] In these tests limestone was injected with the coal through the burners at a Ca/S ratio of 2. Sulfur captures of over 70 percent were achieved. Speculation on why this high level of capture occurred focused on: 1) sorbents would experience longer times at lower temperatures preventing overburning of the stone and allowing more time for sulfation; 2) this burner produced better mixing of the sorbent with combustion gases; and 3) reaction under fuel-rich conditions may allow sulfidation, which is faster than sulfation, to occur. In any case the obvious possibility of simultaneous reductions in SO_2 and NO_x emissions became the focus of on-going research. It became apparent rather quickly that sorbents varied widely in their ability to capture SO_2. It was also noted that a particular sorbent's performance could be varied by altering boiler-related parameters such as injection location and quench rate.[5, 6] The culmination of this research will be the LIMB demonstration at Ohio Edison's Edgewater station beginning in May 1987.

The remainder of this paper will describe the sorbent properties and boiler parameters thought to be critical to a successful LIMB demonstration. It will also discuss additional considerations believed to be important to commercial acceptance of the process. Finally, it will briefly review the sorbent enhancement development studies which have been undertaken.

SORBENT SELECTION

A wide range of sulfur captures have been achieved using different commercially available sorbents. The parameters discussed below are believed to be responsible for these differences.

Sorbent Type and Surface Area

Investigations at EPA's Research Triangle Park (RTP), NC, laboratory have shown that different commercially available limestones and dolomites calcined under identical conditions achieve significantly different maximum surface areas. Figure 1 shows previously reported results[7] of 10 materials screened to a top size of 325 mesh (45 μm) and calcined at 850°C (1562°F) for 30 minutes in a still air environment. The superior performance of dolomites as a group is evident and has been widely observed. It was surprising, however, to note that the maximum surface areas developed by limestones varied by as much as a factor of three. It is assumed that these same stones would also exhibit a range of surface areas and sulfur captures when injected into a furnace environment. Separate studies at the University of Utah by Newton et al.[8] and Harrison et al.[9] have verified the correlation between surface areas produced in these types of calcination studies and SO_2 capture in an experimental furnace.

Experimental evidence also exists to demonstrate that different commercially available calcium-based carbonates and hydroxides vary widely with respect to surface area development and sulfur capture during furnace injection. Table 1 summarizes test results produced in three pilot-scale research efforts: Overmoe et al.,[10] Beittel et al.,[11] and Bortz and Flament.[12] The data in this table show a clear and relatively consistent relationship between the classes of sorbents: dolomitic sorbents are always better than calcitic sorbents, and hydroxides are better than carbonates. Slaughter et al.[13] at the University of Utah demonstrated the same order of reactivities in a smaller isothermal reactor. Both Beittle's and Slaughter's investigations experimentally demonstrated the correlation between surface area and SO_2 capture, as did the work of Borgwardt et al.[14,15]

Experimental evidence compiled thus far strongly implies that limestones vary from one to another in their reactivity with SO_2 after calcination. Still more compelling is the evidence which suggests that much greater SO_2 capture can be achieved by substituting a hydrated sorbent for a carbonate. Although dolomitic carbonates consistently appear to outperform calcitic carbonates and dolomitic hydrates are superior to calcitic hydrates on an equivalent calcium basis, Newton and Pershing[16] have concluded that on an equivalent mass basis dolomitic materials probably offer no significant advantage over calcitic materials. Cal-

cium hydroxide, therefore, appears to be the sorbent of choice among those currently commercially available unless only dolomitic materials are practically available in a given area.

Particle Size and Pore Size Distribution

In addition to sorbent type and surface area, particle size has an important effect on reactivity which recently has been documented by Newton and Pershing,[16] and by Gullett and Blom.[17] Smaller particles are in general chemically more reactive for a given mass because of the increased external surface area they provide. During the sulfation of a sorbent an additional factor comes into play, however. The reaction appears to be limited by product layer buildup and the subsequent inability of SO_2 to diffuse rapidly enough into the particle interior. The shorter diffusion path of smaller particles allows greater SO_2 accessibility and subsequent reaction before product layer buildup slows the reaction.

The distribution of pore sizes in the sorbent particles has also been recognized as important in determining the ultimate utilization.[18] It was originally believed, however, that the finest pore structure achievable would be most beneficial since the finer pore sizes develop as maximum surfaces areas are reached. Recent experimental and modeling studies by Newton and Pershing,[16] and by Simons and Garman[19] have shown that the

finest pores are the first ones to be excluded from the sulfation reaction due to the buildup of reaction product at the pore mouth. This implies that a slightly sintered particle with a less than maximum achievable surface area and a pore size distribution skewed slightly toward the larger diameter pores may be optimal. It is not yet known how to determine the optimal combination of surface area and pore size distribution, nor how to reconcile these results with earlier studies that show reactivity continually increasing with surface area.

Demonstration Sorbent Tests

Since the ability to identify the most reactive sorbent based on fundamental properties is not yet fully realized, candidate sorbents for the LIMB demonstration were tested for reactivity in a number of pilot scale furnaces at EERC, Southern Research Institute (SRI), and the University of Utah. Of the non-dolomitic, calcium-based sorbents commercially available, hydrates consistently have been shown to achieve the highest reactivity and were, therefore, the only group subjected to furnace testing. The results of these tests are shown in Figure 2. Only the gas-fired reactor at the University of Utah was unable to distinguish among the candidate hydrates. The coal-fired reactors at EERC and SRI both showed significant differences in reactivity among the hydrates, and the relative rankings were remarkably similar. In this series of tests hydrate supplied by the Marblehead Lime Company from its River Rouge plant

appeared to be the most reactive and was subsequently chosen for use in the LIMB demonstration at Edgewater.

BOILER CHARACTERISTICS

Due to the critical importance of boiler characteristics on sorbent reactivity and sorbent mixing with combustion gases, a considerable effort was undertaken to characterize the Edgewater boiler.

Method of Determination

The work included flow characterization in a 1:15 scale acrylic model of the boiler, use of a computational boiler code to estimate temperature profiles, and direct measurement of temperature and velocity at selected points in the boiler.

Compilation and evaluation of this information show important implications for sorbent injection. The temperature zone of highest reactivity is located in the upper furnace from a plane just above the nose to a plane farther back in the convective section. A reduction in boiler load moves this zone closer to the boiler nose. Bubble streak flow visualization in the scale model showed that flow velocity increases near the nose, as would be expected, and that the flow is nearly uniform across the width of the boiler. Injection will take place at the plane of the nose in the

high velocity region with sufficient injection velocity to penetrate and distribute the sorbent within the furnace.

Important Factors for Sulfur Capture

One of the primary boiler-related considerations in achieving maximum sulfation of the sorbent is the location of the sulfation temperature window. The reaction of SO_2 with CaO proceeds too slowly to be of interest below approximately 900°C (1650°F). Above about 1250°C (2300°F) the $CaSO_4$ dissociates into its components. The sulfation temperature window for the LIMB process is, therefore, from 900°C to 1250°C. The residence time in the optimum temperature window for the Edgewater boiler is very short, on the order of 1 second, indicating that this boiler will be a rigorous test for sorbent injection.

The boiler quench rate, or the rate at which combustion gases decrease in temperature, is also important because it governs the amount of time the sorbent will have in the sulfation temperature window. Figure 3 shows the relationship between quench rates and time available for sulfation. In this figure a sorbent in a hypothetical boiler with a high quench rate will have a sulfation time of ET_1; considerably less than 1 second. In a boiler with the lower quench rate, the time can be extended to ET_2 or somewhat more than 1 second. The Edgewater boiler is believed to fall within this range of times.

The final factor of major importance is believed to be sorbent mixing with the combustion gases. The design of an effective sorbent injection system will ensure rapid dispersion at approximately 1250°C (2300°F) for maximum reactivity and time in the reaction zone. Based on present understanding, development of an optimum injector design is an iterative process based on use of a combination of predictive tools and experimental investigation aimed at getting an even distribution of sorbent across a plane in the boiler. Based on boiler geometry and operating characteristics, a number of practical injection designs can be considered and refined using predictive techniques. The most promising injection combinations can then be evaluated experimentally using scaled down boiler models to select an injection scheme that will give an optimum mixing pattern in the boiler.

Based on the Edgewater boiler geometry, boiler combustion air limitations, and expected injection patterns, a flexible injection scheme has been proposed which will provide the ability to inject at three levels in the boiler: at the nose level, and two levels above the nose (Figure 4). Only two injection levels will be operable at one time. Each level will have a row of eight injector ports on the front wall; the middle level will also have two injector ports on each side wall. Provision has been made for variable injection velocities and the ability to tilt the injectors at the two upper levels 30° down from horizontal.

Important Factors for Commercialization

Demonstrating an acceptable level of NO_x and SO_2 reduction is, unfortunately, not sufficient to make the LIMB process commercially attractive. In addition, the process must not have a negative effect on the particulate collection system, must not significantly reduce boiler efficiency by creating fouling and slagging problems, and must not create a disposable solid waste which violates the standards set by the Resource Conservation and Recovery Act (RCRA).

With respect to particulate control one primary consideration is the increased particulate loading that accompanies sorbent injection. Depending upon the original ash and sulfur content of the coal, application of LIMB may increase particulate loading by a factor of two to three. These effects are of special concern in retrofit applications where existing electrostatic precipitators (ESPs) are designed to meet applicable mass emission rate and visibility regulations without sorbent addition.

The Edgewater ESP is unique for boilers of the Edgewater vintage in that it was retrofitted to the unit in 1982 and is substantially oversized for its present duty. Estimates indicate that existing emission standards can be met even with LIMB addition with this ESP. Other boiler LIMB retrofits may, however, have to consider construction of additional ESP surface area.

The second major factor affecting ESP efficiency is the resistivity of the ash. As ash resistivity increases, ESP efficiency decreases. The removal of SO_2 from the flue gas tends to raise the resistivity so countermeasures may need to be considered. It is believed that incorporation of precharging or gas conditioning will eliminate the problem, but this remains to be demonstrated at Edgewater. In an earlier demonstration of LIMB on an industrial boiler Conoco showed that gas conditioning by humidification was sufficient to maintain ESP efficiency.(20)

The deposition of excessive amounts of solids in various parts of the boiler through the processes of fouling and slagging can drastically reduce the efficiency of a boiler. These problems can be exacerbated by increased quantities of ash or sorbent and changes in the ash chemistry. While increases in solids loading will, of necessity, accompany LIMB, the result of the change in ash chemistry during sorbent injection will depend on the original chemistry of the coal ash. The effect could be either positive or negative depending on the composition of the coal ash. The Conoco study(20) showed that, while solids deposition in the radiant and screen tube sections of the boiler increased as expected during sorbent injection, the modification in ash composition resulted in deposits more friable and easily removed by standard soot blowing techniques. No decrease in boiler efficiency was observed due to deposition.

The final area of consideration for commercialization is ash handling and disposal. Application of LIMB creates an additional waste load and

a change in ash properties. The present Edgewater waste handling and disposal system is a dry system in which ash is pneumatically removed from the ESP bottom to an ash silo, sprayed with a small amount of water in a pug mill for dust control, and trucked to a nearby landfill. In order to verify that the LIMB ash could be processed in the existing equipment, several truckloads of ash material generated during lime injection at a Canadian power plant were transported to the Edgewater plant and processed through the silo pug mill system. The Canadian material was similar to the ash expected at Edgewater, but had a slightly lower free lime content. It was found that the lime in the ash could be neutralized (hydrated) in the pug mill and a dust-free material could be produced for truck hauling to a landfill. Control of water amount and rate were found to be critical to avoid pug mill pluggage and hardening of the material in the truck.

Testing of LIMB waste under conditions specified in RCRA showed (Table 2) that leachable toxic materials were far below levels considered to be hazardous, that rain runoff from the stored material would appear to meet required pH levels, and that ignitability and reactivity are not a problem. Current plans are for the LIMB-modified ash to be disposed of in an existing landfill but separated from conventional ash storage for observation and testing.

ECONOMIC COMPARISON

In addition to technical considerations, the LIMB process must also be shown to be economically competitive with other SO_2 control processes. The cost modeling performed to date compares the LIMB process to wet and dry FGD on a $/ton of SO_2 removed basis.[21] The bases for comparison are coal sulfur content, boiler capacity factor, sorbent cost, boiler size, and remaining boiler life.

The range of coal sulfur levels considered was from 1.5 to 3.0 percent with a midpoint of 2.2 percent. This represents the range of sulfur contents to be used at the Edgewater demonstration. A 1969 survey by the Federal Power Commission of U.S. power plants showed that the weighted average of coal sulfur contents was 2.6 percent. A more recent data base (MEGABASE) of coals used by power plants in the eastern 31 states shows an average sulfur content of 2.0 percent, justifying the 2.2 percent level chosen for the base case in this study.

MEGABASE data revealed that the average capacity factor for uncontrolled boilers was 50 percent and this was accepted for the base case. The upper limit was set at 65 percent corresponding to a typical capacity factor for a base loaded plant as suggested by the Electric Power Research Institute.[22] A lower limit of 35 percent was chosen for symmetry about the base case.

The cost of hydrated lime used in the base case was set at $71/ton ($64/tonne) reflecting an originally quoted price for delivered sorbent at the Edgewater plant. This consists of a typical F.O.B. cost of about $50/ton ($45/tonne) and 200 miles (322 km) of truck transportation. The upper and lower bounds were set at $55/ton ($50/tonne) and $85/ton ($77/tonne), respectively, to reflect varying F.O.B. and transporation costs. A similar cost was indicated for the pebble lime used as a sorbent for dry FGD. The base case limestone cost for wet FGD was set at $15/ton ($14/tonne) with upper and lower bounds of $12/ton ($11/tonne) and $18/ton ($16/tonne), respectively.

Using MEGABASE data once again the average boiler size of uncontrolled units was determined to be in the 200 to 300 MWe range. 300 MWe was used for the base case with a range from 100 to 500 MWe.

A remaining unit life of 15 years was selected for the base case as being representative of retrofit candidates, and a range of 10 to 20 years was arbitrarily chosen for symmetry about the base. The base case level of SO_2 control for LIMB was set at 50 percent since this is the target level. The level was set at 84 percent for both FGD cases corresponding to New Source Performance Standards for the 2.2 percent coal selected for the base case.

Results of the modeling were presented as the relative sensitivities of the three control technologies to the factors discussed above. LIMB at

50 percent removal exhibits a lower cost per ton of SO_2 removed than both wet and dry FGD up to about 2.6 percent sulfur. Beyond this point there is a crossover, with dry FGD showing a slight advantage over LIMB.

The effect of capacity factor on all three technologies is to decrease control costs as capacity factor increases. Because of their higher capital component the FGD costs decrease more rapidly than LIMB. Since more total SO_2 is removed at higher capacity factors, the larger capital costs of the FGD processes become a smaller portion of the total control cost expressed in $/ton of SO_2 removed. LIMB is more cost effective through the full range of capacity factors considered, although the differences narrow significantly at the higher levels.

Control costs increase as sorbent costs increase for all three technologies as expected. This effect is more pronounced for LIMB, however, since it is more operation and maintenance (O&M) cost intensive. Nevertheless, LIMB remains the least expensive through the full range of sorbent costs included in the model.

The control costs of all three technologies decrease as boiler size increases due to economics of scale. The effect of size on costs for FGD is more pronounced since these technologies are more capital cost intensive, but LIMB remains least expensive through the range of boiler sizes.

For both wet and dry FGD, there is a decline in control cost up to a book life of between 15 and 20 years, after which the costs rise monotonically. The reason for this is that the control cost consists of both a levelized capital carrying charge component and a levelized O&M cost component. As book life is increased, the carrying charge factor decreases, while the O&M levelization factor, which is a function of inflation and discount rates, increases. At about the 15 to 20 year time frame, there is a crossover point at which the rise in O&M costs offsets the decline in carrying charge rate, and unit control costs begin to slowly increase with book life. With LIMB, which is more O&M cost intensive, the decline in carrying charge is always offset by the increase in O&M over the range of book life considered. Once again the cost of LIMB remains below the other technologies throughout.

Briefly then, the base case costs for wet FGD, dry FGD, and LIMB are $1,337/ton ($1,213/tonne), $1,120/ton ($1,016/tonne), and $997/ton ($904/tonne), respectively. The sensitivity analysis shows that LIMB's cost effectiveness improves relative to wet and dry FGD with decreases in: 1) boiler size; 2) coal sulfur content; 3) capacity factor; 4) remaining unit life; and 5) sorbent cost. Finally, the analysis shows that both wet and dry FGD are more capital cost intensive than LIMB, whereas LIMB is more dependent on O&M costs.

MODIFIED SORBENTS

In an attempt to improve upon the reactivity of commercially available calcium hydroxide sorbents, both in-house and extramural research has been directed toward the issue. Efforts thus far have addressed the use of chemical promoters added to the sorbent, the effects of calcination and hydration parameters on sorbent reactivity, and the use of surfactants added to the water of hydration.

The ability of certain chemical species to enhance the reactivity of sorbents was the focus of research recently conducted at EERC.[23] Preliminary studies had shown that chromium was a highly effective promoter but its use in commercial applications is prohibited by economic and environmental considerations. The use of iron compounds was considered because the presence of iron had previously been shown to increase SO_2 capture in fluidized bed combustion studies. Within the time and temperature constraints of the LIMB process, however, it proved ineffective. Alkali metals, particularly sodium, were the final group of compounds found to be highly effective in promoting sulfur capture with increases in reactivity of up to 50 percent being observed during gas-fired tests. The sodium appears to produce its effect by vaporization and condensation on the sorbent, followed by enhanced sintering and the formation of a low-melting, liquid layer on the sorbent surface. During coal-fired testing, however, virtually all of the enhanced reactivity is lost. Because the mineral matter in coal provides many more sites than the sorbent for the

sodium to condense upon, most of the sodium is lost to the coal ash. No method of adding sodium to the sorbent could be identified which would circumvent deactivation by the coal ash, and the use of chemical promoters for enhancing reactivity has been abandoned for the present.

A second area of interest addressed in in-house studies at EPA was the effect of calcination and hydration parameters on the reactivity of calcium hydroxides with SO_2. Research conducted during the 1940's and 1950's, much of it sponsored by the National Lime Association, showed that these parameters could affect hydration rates and particle settling rates, but the effect on reactivity of the resulting materials with SO_2 was not addressed. Recent in-house studies determined the effect of parent lime particle size, extent of calcination, and hydration water temperature on the reactivity of the resulting hydroxides with SO_2.[24] Preliminary results indicated that reactivity of the hydroxides increases with: 1) decreasing particle size of parent lime; 2) decreasing calcination time; and 3) increasing temperature of water of hydration. Reactivity increases of 20 to 25 percent were observed, but the results remain to be verified at a larger scale and at conditions more nearly resembling those of commercial facilities.

The third approach addressed by EPA research involved the addition of surfactants, more specifically dispersants, to the water of hydration during the production of calcium hydroxide. It was hypothesized that these additives might serve as structural modifiers to the hydrate, as

distinguished from the chemical promoters discussed above. It has already been noted that decreasing sorbent particle size increases the reactivity of all sorbents. It has also been shown that the tendency of hydrate particles to agglomerate effectively increases the particle size presented to the sulfation reaction and reduces their reactivity.[17] If the use of dispersants in the water of hydration could reduce agglomeration, then a particle size more nearly approaching the fundamental hydrate crystal size could be made available for reaction. Laboratory-scale studies have shown that additions of calcium lignosulfonate to the hydration water significantly reduce the size of agglomerates which are formed and increase the reactivity of hydrates with SO_2 by about 20 percent.[25] This effect is the focus of ongoing research at EPA.

SUMMARY

In preparation for the 1987 LIMB demonstration at Ohio Edison's Edgewater plant an extensive amount of research has been conducted. It appears that calcium hydroxides are the sorbents of choice among the commercially available calcium-based sorbents. The effect and interrelationship of fundamental sorbent properties are fairly well understood and continue to be topics of investigation. The boiler conditions necessary for effective SO_2 capture have been defined, and the Edgewater boiler has been well characterized with respect to sulfation temperature window, quench rate, flow patterns, and injection location. An effective sorbent injection system has been designed and is being installed.

The effects of sorbent injection on boiler efficiency, particulate collection, and solid waste handling and disposal have been studied, and negative effects can apparently be remedied by available techniques. Cost comparisons of LIMB with other SO_2 control technologies, to the extent that they are comparable, show the process to hold an impressive advantage.

Finally, studies have been conducted and are continuing which suggest that commercially available sorbents can be modified to achieve increased reactivity with SO_2. Changes in calcination and hydration conditions, and the addition of dispersants to the water of hydration, have shown promise and await large scale testing.

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TABLE 1. PERCENT SO_2 CAPTURES ACHIEVED WITH DIFFERENT CLASSES OF CALCIUM-BASED SORBENTS

Reference	Approximate Injection Temperature, °C	Percent SO_2 Capture at Ca/S = 2			
		Limestone	Calcium Hydroxide	Dolomite	Pressure Hydrated Dolomite
Overmoe et al.[17]	1230	30	42-48	57	74
Beittle et al.[18]	1200	40	50-60	55	70-80
Bortz & Flament[19]	1200	30-40	65-80	--	--

TABLE 2. LEACHATE DATA FOR SIMULATED LIMB DEMONSTRATION WASTE PRODUCTS

	Allowable Limit Per RCRA*	Demo Coal/ Hydrate A*	Demo Coal/ Hydrate B*
Arsenic	5	0.0145	0.0210
Barium	100	4.11	4.24
Cadmium	1	0.00095	<0.0005
Chromium	5	0.0394	0.0240
Lead	5	<0.0030	0.0045
Mercury	0.2	<0.0003	<0.0003
Selenium	1	0.0296	0.0228
Silver	5	<0.0005	<0.0005
pH	12.5	(12.4/12.2)†	(12.4/12.2)†

* Concentration in extract in mg/l.
† Before/after acetic acid addition per the Extraction Procedure (EP) Toxicity Test.

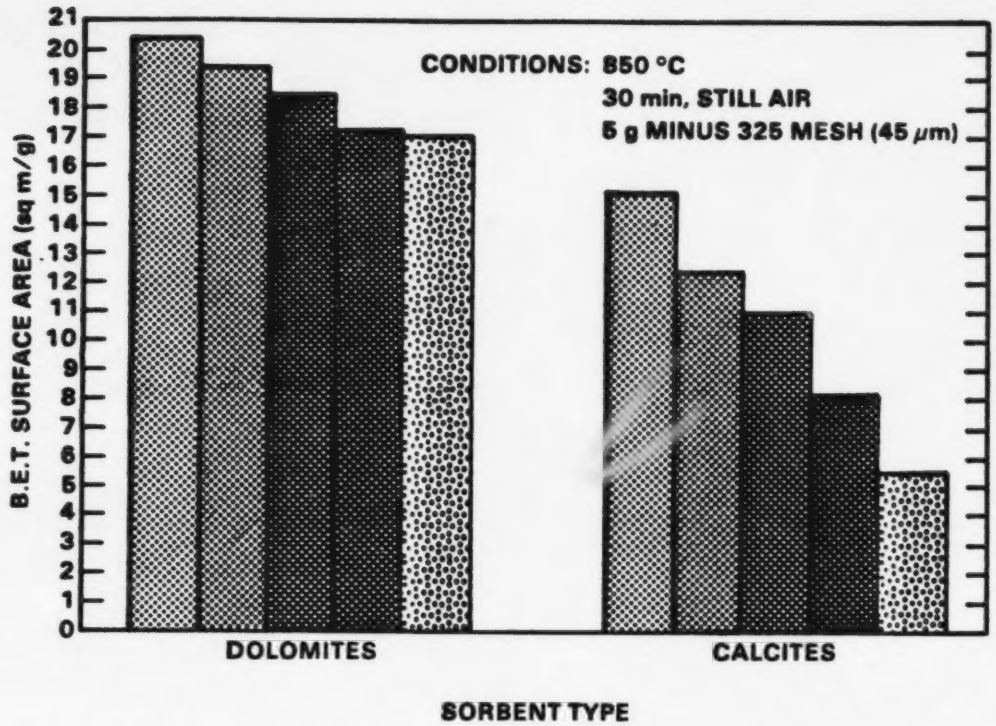

Figure 1. Batch calcinations.

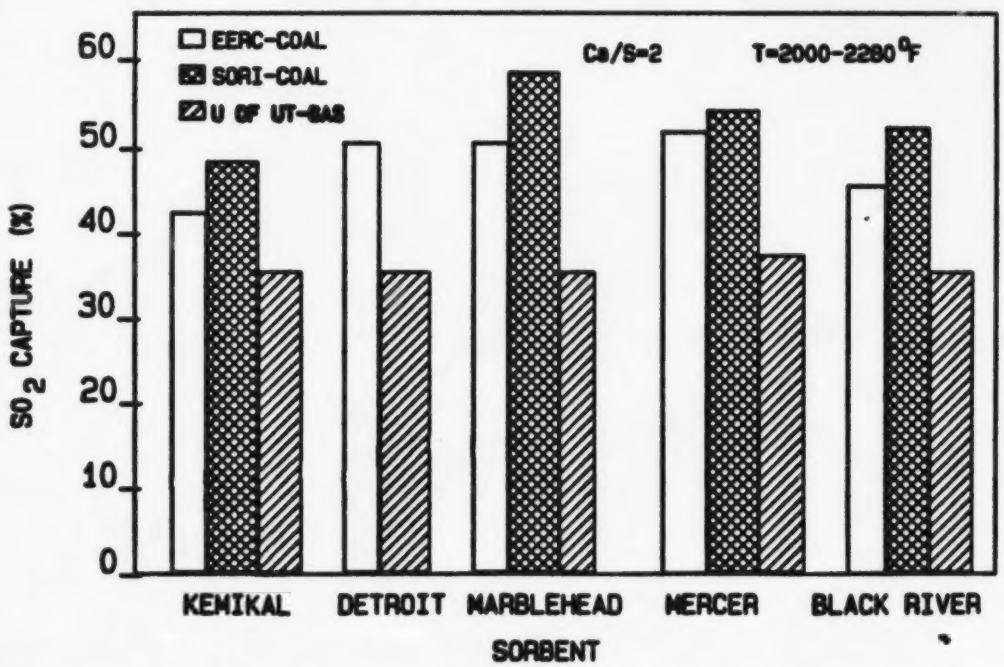

Figure 2. Demonstration sorbent testing.

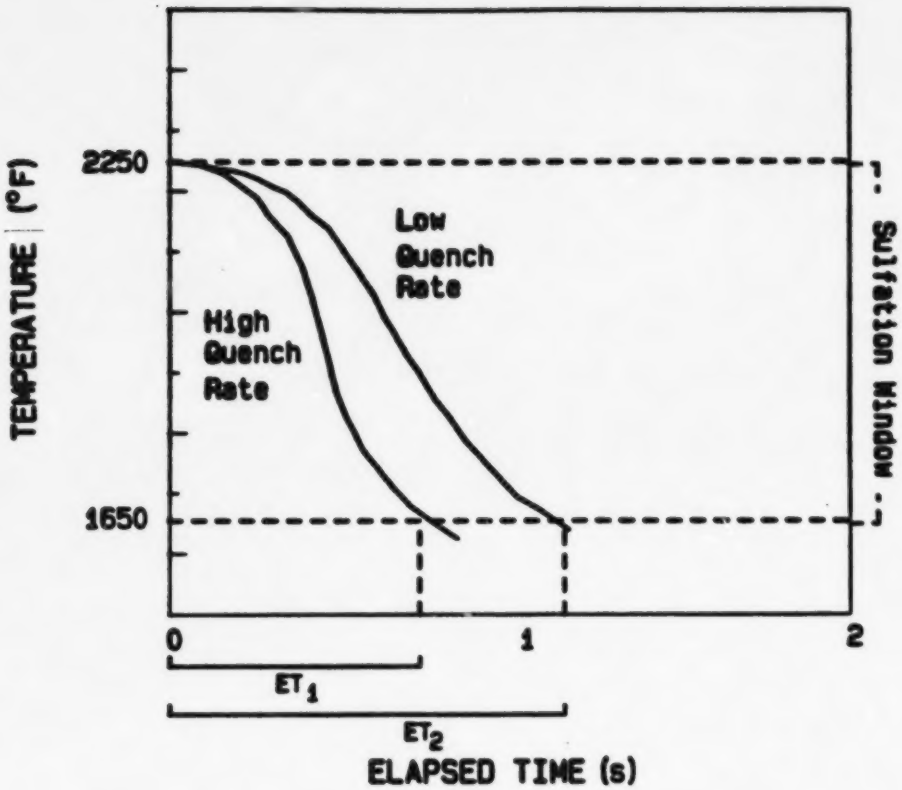

Figure 3. Effect of quench rate on residence time.

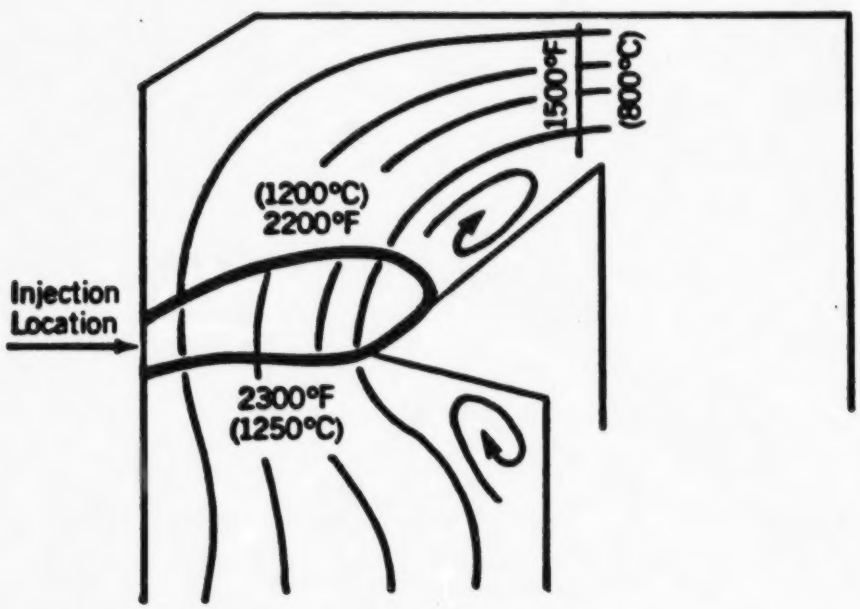

Figure 4. Location of sulfation temperature window and injection location.